How the phenyl rings (benzene) act as building blocks in the π conjugated polymers

J.-H. Guo[1], M. Magnuson[1], C. Såthe[1], J. Nordgren[1], L. Yang[2], Y. Luo[2], H. Ågren[2], K. Xing[2], N. Johansson[2], W.R. Salaneck[2], R. Daik[3], and W.J. Feast[3]

[1]Department of Physics, Uppsala University, Box 530, 751 21 Uppsala, Sweden
[2]Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden
[3]IRC in polymer Science and Technology, Durham University South Road, Durham DH1 3LE, United Kingdom

INTRODUCTION

Organic conjugated polymers have the electronic structure of semiconductors and can be doped to become good conductors [1]. Conjugated polymers are now used as active materials in a wide variety of prototype applications such as light emitting diodes [2] and organic transistors [3,4]. Most of the interesting chemistry and physics of conjugated polymers is associated with the details of the electronic structure at the valence and conduction band edges and, in this connection, various electron spectroscopies can be used as tools for diagnosis of the relevant electronic and geometric properties.

The x-ray emission (XE) technique provides a means of extracting chemical information in the form of molecular orbital (MO) population and local density distribution of certain symmetries owing to the dipole character of the radiative decay and the localization of core-hole states. The resonance inelastic x-ray scattering (RIXS) measurements are symmetry selective at high resolution.

X-ray emission occurs due to an interaction of incident x-ray photons with a target consisting of atoms, molecules or a solid. The traget is excited from the ground state $|o>$ to a core excited state $|i>$ by absorption of an incoming x-ray photon (γ) with specific frequency, wave vector and polarization vector. The core excited state is metastable due to vacuum zero vibrations or interelectron Coulomb interaction and can therefore decay to final states $|f>$ in two different ways, by emitting x-ray photons or by emitting high-energy Auger electrons; $M + \gamma \rightarrow M_i \rightarrow M_f + \gamma'$ and $M + \gamma \rightarrow M_i \rightarrow M_f + e^-$ constituting the radiative, respectively, non-radiative decay channels of the x-ray scattering process. When the frequency of the incident x-ray photons is tuned below or closely above the core ionization threshold resonant core excitation takes place. It is natural to refer to this case as to resonant x-ray scattering or x-ray Raman scattering.
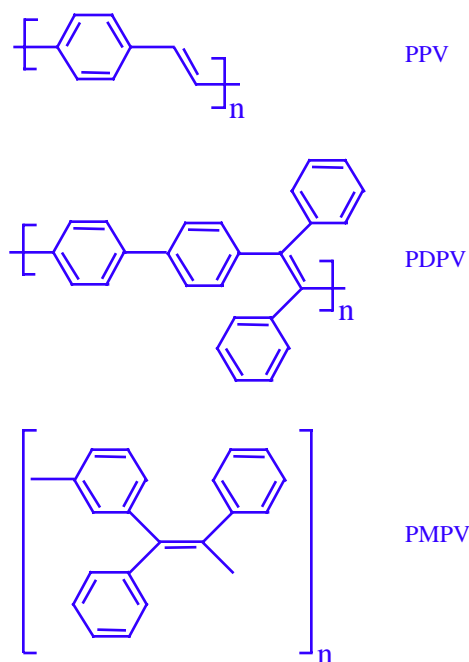

Figure 1. Schematic diagrams of poly(phenylenevinylene)s.

In the present work we probe the electronic structure of a set of poly(phenylenevinylene)s (See in Fig. 1): poly(phenylenevinylene) (PPV), poly(4,4'-diphenylenediphenylvinylene) (PDPV) and,

poly(1,3-phenylenediphenylvinylene) (PMPV), using x-ray absorption and emission spectroscopies which have been shown to be powerful techniques for studying electronic structures in other contexts. These compounds are made up of six membered carbocyclic aromatic rings connected by short hydrocarbon bridges.

EXPERIMENT

The experiments were performed at beamline 7.0 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [5]. Near edge x-ray absorption fine structure (NEXAFS) spectra were obtained by measuring the total electron yield from the sample. The resolution of the monochromator was set to 0.15 eV. The XAS spectra were normalized to the incident photon current using a clean gold mesh to correct for intensity fluctuation in the photon beam. The XE spectra were recorded using a high-resolution grazing-incidence x-ray fluorescence spectrometer [6]. During the XE measurements, the resolution of the beamline was 0.25 eV, and the resolution of the fluorescence spectrometer was set to 0.5 eV for C K emission.

The PPV sample was prepared from a soluble THT-leaving group precursor polymer [7]. The precursor was spin-coated onto Si(110) wafers, and converted to PPV at 240°C for 10 hours under a mild vacuum of 5×10^{-6} mbar. The PDPV and PMPV samples were prepared by McMurry coupling of 4,4'-dibenzoylbiphenyl and metadibenzoylbenzene respectively, following the method described by Millichamp [8]. The crude products were purified by equilibrium fractionation (chloroform solven/heptane non-solvent @ 20°C) following the technique described previously [9]. The PMPV and PDPV polymers were spin-coated from 2 mg/ml polymer/chloroform solution onto Si(110) substrates. All the samples were sealed in an N_2 atmosphere in glass and has been exposed to air for very short time just before they were introduced into the vacuum system for XE measurement.

RESULTS

The non-resonant XE spectra of the poly(phenylenevinylene)s excited with 310 eV photon-energy aligned together with the NEXAFS spectra are presented in Figure 2 (left). The spectrum of benzene, the main part of which is well understood [10], is also included for comparison. The energy scales of the spectra have been aligned by using the elastic peak in the RIXS spectra presented at the right side in Figure 2. The normal x-ray emission spectra of all systems can be grossly subdivided into 6 bands in the energy range from 265 to 283 eV. The band patterns of the poly(phenylenevinylene)s resemble those of benzene.

Benzene has ground state D_{6h} symmetry with 9 outer valence MO levels with intensity in the XE spectra. The six bands, which are denoted by the italic letters from *A* to *F* from the high energy side, can thus be assigned to x-ray transitions involving the $1e_{1g}$, $3e_{2g}+1a_{2u}$, $3e_{1u}+1b_{2u}+2b_{1u}$, $3a_{1g}$, $2e_{2g}$, $2e_{1u}$ MO's, respectively. The latter two bands are weak because of the 2s character of the corresponding MOs and presumably also because of the breakdown of the molecular orbital picture with accompanying correlation state splittings [11].

The (RIXS) spectra were recorded by tuning the incident x-ray photon beam to the first π^* resonance (284.8 eV) and are presented in Figure 2 (right). Similarly to the nonresonant case, the resonant spectra of poly(phenylenevinylene)s demonstrate a strong similarity with the resonant spectrum of benzene.
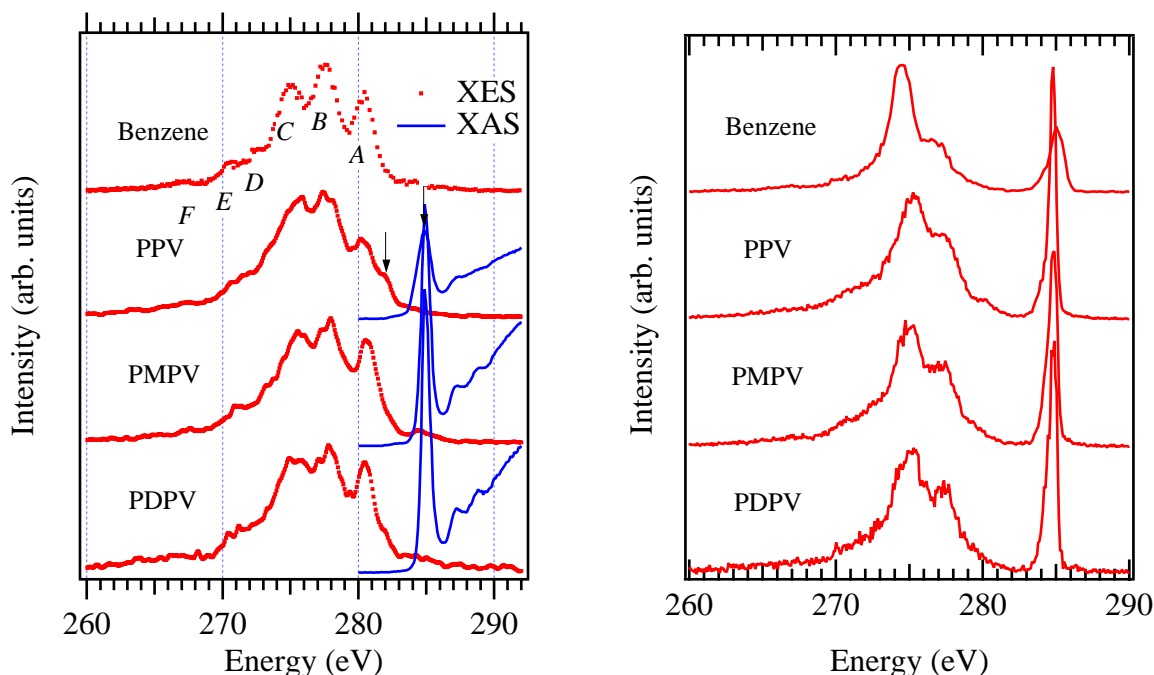
Figure 2. Non-resonant C *K* x-ray emission spectra excited at 284.5 eV together with x-ray absorption spectra of polymers (left) and resonant C *K* x-ray emission spectra excited at 310 eV (right).

DISCUSSION

The lowest unoccupied molecular orbital (LUMO) of C_6H_6 is $1e_{2u}$ (using ground state D_{6h} point group symmetry). When the incident x-ray is tuned to $1e_{2u}$, only electrons occupying the ungerade MO's can fill up the C_{1s} hole according to the parity selection rule for resonant x-ray scattering (gerade - gerade and ungerade-ungerade). This assumes that the core excited state maintains the same symmetry as the ground state D_{6h} . In particular, the HOMO $1e_{1g}$ level, corresponding to emission energy around 280 eV will be symmetry forbidden. This is the reason that the emission band *A* of highest energy in the nonresonant spectrum disappears in the resonant spectrum. The band *B* at 278 eV in the nonresonant spectrum, which originates in transition from the $3e_{2g}+1a_{2u}$ levels, should also be depleted in the resonant case due to symmetry selection. Although it does show reduced intensity, there is a significant intensity remaining, which was argued as being due to a final state vibronic coupling effect [10].

For the polymers, there exists no symmetry at all, and one could expect from this point of view that the resonant and nonresonant XE spectra would be similar. On the other hand if the vinylene groups exert only small perturbations on the phenyl ring the local electronic structure of the benzene molecule can remain intact and since the x-ray process is local one can then argue that an "effective" symmetry selection can be restored. The experimental spectra for polymers, indeed show benzene-like features also in the resonant case, with the band *A* intensity considerably reduced. The restoration of the effective symmetry selection (as well as the benzene similarity) must be ascribed to *channel interference*; the x-ray scattering of the different close-lying core-hole states interfere in such a way that the total signal is depleted. To estimate the chemical splitting of the $C_{1s} \rightarrow \pi^*$ transitions from the phenyl ring and vinylene core sites, a static exchange (STEX) calculation has been carried out for PPV. It gives a maximum for the energy splittings of 0.18 eV for the $C_{1s} \rightarrow \pi^*$ excitations corresponding to different core sites (actually also for the C_{1s} ionization potentials).

We note that by combining the resonant and the nonresonant XE spectra, one can obtain the band gap of the polymers. It equals the energy difference between the elastic peak in the RIXS spectrum and the front edge of the non-resonant XE spectrum. They are close to 2.8 eV for all the PPV, PMPV, and PDPV polymers. These quantities seem to fall in between the values obtained from optical absorption spectroscopy [12], 2.45 eV for PPV, and ultraviolet photoelectron spectroscopy 3.1 eV for PPV [13]. The differences might refer to the different broadening mechanisms for the bands and to the actual identification of the adiabatic or vertical transition energies which might come out differently in the different kinds of spectroscopies.

CONCLUSIONS
The conspicuous resemblance with benzene in both resonant and nonresonant x-ray emission spectra indicates no major electronic or geometric structure changes in the phenyl rings connecting with a vinylene group, and indicates also that the phenyl ring works as an excellent building block for these spectra. The benzene-like features in the RIXS spectra of the polymers are interpreted as the result of a strong channel interference. Only by accounting for this interference the π-electron emission derived from the forbidden e_{1g} level in benzene vanishes for the polymers.

The aspect of an alternative way to determine the band gap, as well as the building block character and the particular interference effects here studied, might be worth exploiting for other types of polymers as possible diagnostic tools.

ACKNOWLEDGMENTS

REFERENCES
1. C.K. Chiang, C.R. Fincher, Y.W. Park, *et al.*, Phys. Rev. Lett. **39**, 1098 (1977).
2. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, *et al.*, Nature **347**, 539 (1990).
3. J.H. Burroughes, C.A. Jones, and R.H. Friend, Nature **335**, 137 (1988).
4. F. Garnier, G. Horowitz, X. Peng, *et al.*, Adv. Mater. **2**, 592 (1990).
5. T. Warwick, P. Heimann, D. Mossessian, *et al.*, Rev. Sci. Instr. **66**, 2037 (1995).
6. J. Nordgren, G. Bray, S. Cramm, *et al.*, Rev. Sci. Instr. **60**, 1690 (1989).
7. P.L. Burn, D.D.C. Bradley, *et al.*, J. Chem. Soc. Perkin Trans. **1**, 3225 (1992).
8. W.J. Feast and I.S. Millichamp, Polym. Commun. **24**, 102 (1983).
9. F. Cacialli, R. Daik, *et al.*, Philos. Trans. R. Soc. London, Ser. A **355**, 707 (1994).
10. P. Skytt, J.-H. Guo, N. Wassdahl, et al., Phys. Rev. A **52**, 3572 (1995).
11. L.S. Cederbaum, W. Domcke, J. Schirmer, et al., J. Chem. Phys. **69**, 1591 (1978).
12. J.L. Bredas, J. Cornil, and A.J. Heeger, Adv. Mater. **00**, 000 (1996).
13. M. Fahlman, M. Lögdlund, S. Stafström, et al., Macromolecules **28**, 1959 (1995).

Principal investigator: E. Joseph Nordgren, Department of Physics, Uppsala University. E-mail: joseph@fysik.uu.se. Telephone: +46 18 4713554.